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# Effect of Surfactant Headgroup on Low-Fluorine-Content $CO_2$-Philic Hybrid Surfactants

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## Abstract

The article addresses the role of surfactant headgroup structure on hybrid surfactant performance for water-in-$CO_2$ (w/c) microemulsion stabilisation. The synthetic procedure, aqueous properties, and phase behaviour of a new hybrid sulfoglutarate surfactant are described. The sulfoglutarate version has an extra methylene group incorporated into the hydrophilic headgroup. The related hydrocarbon (AOT14 and AOT14GLU) and fluorocarbon (di-CF2 and di-CF2GLU) surfactants were used to form w/c microemulsions. For these two groups, the aqueous properties and w/c phase stability of both sulfoglutarates and sulfosuccinates were found to be similar. The newly synthesized hybrid CF2/AOT14GLU (sodium (*4H,4H,5H,5H,5H*-pentafluoropentyl-2,2-dimethyl-1-propyl)-2-sulfoglutarate) proved to be more efficient than the normal sulfosuccinate, hybrid CF2/AOT14 in terms of the aqueous behaviour and w/c phase stability. Hybrid CF2/AOT14GLU more effectively decreased the air-water surface tension by ~ 2 mN $m^{-1}$ and lowering the cloud pressures on $CO_2$ by ~150 bar.



Keywords: $CO_2$-philic surfactant, supercritical carbon dioxide (sc-$CO_2$), w/c microemulsions, surfactant headgroup

## 1. Introduction

Supercritical carbon dioxide (sc-$CO_2$) is considered a desirable solvent for green materials and chemical processing [1-2], so sc-$CO_2$ has been used for various applications [3-4] and interest still remains high today [5-8]. As such $CO_2$ is a nonpolar molecule with low dielectric constant and solubility parameter, which makes it unsuitable for dissolving polar and high-molecular-weight materials [9]. These weak solvent properties undoubtedly limit the practical applications of sc-$CO_2$. One effective approach to overcome these problems is to use $CO_2$-philic surfactants to stabilize microemulsion phases, for example, water-in-$CO_2$ (w/c) microemulsions. The formation of reverse micelles with water pools inside bulk $CO_2$ provides a microenvironment for materials which are otherwise sparingly soluble or insoluble in $CO_2$, whereas nonpolar materials are solubilized in the $CO_2$-continuous phase [10-12].

Fluorination is considered a key feature for generating $CO_2$-philic surfactants [13, 14]. An investigation using several fluorinated analogues of the common anionic surfactant Aerosol-OT (AOT) shows that an increase in the level of surfactant chain fluorination leads to a decrease in the limiting air-water (a/w) aqueous surface tension ($\gamma_{cmc}$) and a decrease in the phase transition pressure of w/c microemulsions; w/c phase cloud pressure ($P_{trans}$) [15]. However, concerns have been raised because the use of long fluorocarbon chains represents an environmental threat. These issues have been addressed using low F-content hybrid surfactants, where separate fluorocarbon and hydrocarbon chains are chemically bonded to the same hydrophilic headgroup to generating more environmentally-responsible $CO_2$-philic surfactants [16, 17].

The role of the surfactant chemical structure in w/c phase stability has been a central issue in $CO_2$ studies and research has been conducted to determine how changes in surfactant molecular structure can affect physicochemical properties of surfactant aqueous solutions and w/c phase stability [13, 18-21]. A traditional concept of the molecular packing parameter (p)

[22] has been widely invoked to explain the correlation between the molecular structure and the surfactant self-assembly. This geometric parameter is defined as p= $v_0 / a_e l_0$ and includes the contributions of the volume ($v_0$) and length ($l_0$) of the surfactant tail and the interfacial area each surfactant molecule occupies ($a_e$) (which is referred to as the headgroup area in most cases).

Studies using double chain anionic surfactants have been devoted to the effect of structural modifications of the surfactant chains with limited surface tension ability, w/c phase stability, and surfactant solubilizing power [15, 23-27]. Branching, methylation, and fluorination of the chain tips have been shown to induce more favorable tail-$CO_2$ interactions which improve $CO_2$ compatibility [28, 29]. A study on hybrid surfactants has shown that for a constant headgroup type and fluorocarbon chain structure the surfactant performance is notably affected by modification of the hydrocarbon $CO_2$-philic chain structure. Trends in the concentration at which the surfactant molecules started to aggregate into micelles i.e. critical micelle concentration (cmc), the effective area occupied per surfactant molecule at the cmc ($A_{cmc}$), and w/c phase stability were found to link closely with the degree of chain branching, and this can be ranked using an empirical branching factor [30]. A convenient way to rank the effectiveness of surfactants in w/c systems is using the molar solubilization ratio *w* = [water]/[surfactant]: under equivalent P and T conditions, hence, the higher *w* the more effective the surfactant. The hydrophilic headgroup chemical structure has not been systemically studied, mainly because of a lack of suitable compounds; hence, most studies focused on the effects of counterions and headgroup polarity [31-34]. The most relevant work [15, 23, 35] investigated glutarate analogues of the normal sulfosuccinate surfactant.

Sulfoglutarate surfactants (denoted as GLU) were obtained using fluorinated AOT-analogues, for example sodium bis (*1H, 1H, 5H*-octafluoropentyl)-2-sulfosuccinate (di-HCF4;

$\gamma_{cmc}$ = 26.8 mN $m^{-1}$, $P_{trans}$ = 193 bar; *w* = 10 at 25°C) and the related compound sodium bis (*1H, 1H, 5H*-octafluoropentyl)-2-sulfoglutaconate (di-HCF4GLU; $\gamma_{cmc}$ = 25.4 mN $m^{-1}$, $P_{trans}$ = 181 bar; *w* = 10 at 25°C) [15, 23]. Changing sulfosuccinate headgroup for sulfoglutarate increases the hydrophobicity (cmc) and surface-tension-lowering ability, whereas only a subtle change on the $A_{cmc}$ is observed. There is also a slight enhancement of the w/c phase stability with the sulfoglutarate surfactant. Another highly interesting observation with sulfoglutarate surfactants was reported by Sagisaka et al. [36-39] using two related compounds: sulfosuccinate nFS$(EO)_2$ and sulfoglutarate nFG$(EO)_2$ (n = 4, 6, 8). Visual observation and UV-Visible measurements, with the probe dye methyl orange (MO) as a tracer, showed that sulfoglutarate attains higher solubilizing power for w/c microemulsions in $CO_2$ than the sulfosuccinates. Moreover, 4FG$(EO)_2$ (sodium 1,5 bis [(*1H, 1H, 2H, 2H*-perfluorohexyl)oxy]-1,5-dioxopentane-2-sulfonate) has the highest solubilizing power *w* reported to date (*w* ~ 80), which is a significant improvement over other known $CO_2$-philic surfactants.

Using the glutarate analogues of AOT and di-C6SS, which are denoted as AOTGLU and di-C6GLU, respectively, Nave et al. [35] showed that sulfoglutarate and sulfosuccinate surfactants have notably similar aqueous properties, e.g., critical micelle concentration, cmc, $\gamma_{cmc}$ and microemulsion phase stability. Sagisaka et al. [29] also reported the effect of an additional –$CH_2$- spacer on surfactant solution physicochemical properties with two series of highly branched AOT analogue surfactants: di-$BC_nSS$ (sulfosuccinate type) and di-$BC_nSG$ (sulfoglutarate type). In most cases, for hydrocarbon surfactants a modification of the hydrophilic headgroup exerts a weaker effect on the limiting surface tension than for analogous fluorinated surfactants.

Following on from the previous work, this paper aims to investigate the effect of hydrophilic headgroup modification on the performance of novel hybrid sulfoglutarate surfactant for w/c microemulsions stabilization. The glutarate analogue of the hybrid sulfosuccinate surfactant

was synthesized, and the performance was investigated. To minimize the fluorination, in this work the fluorocarbon chain of the hybrid surfactant was fixed using the low-fluorine-content di-CF2 tail [40], whereas the hydrocarbon chain is an AOT14 tail (Table 1), which is the di-chain analogue of the $CO_2$-soluble tri-chain TC14 (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate) surfactant [41]. The performance of the related hydrocarbon and fluorinated surfactants are included. The chemical structures of hybrid, hydrocarbon, and fluorinated sulfoglutarate surfactants, which are denoted as hybrid CF2/AOT14GLU, AOT14GLU, and di-CF2GLU, respectively, and the normal sulfosuccinate, are provided in Table 1. Sulfosuccinates and sulfoglutarates differ in only the headgroup structures: with the addition of an extra $–CH_2-$ spacer on the hydrophilic part, so that sulfoglutarate surfactants now have a symmetrical headgroup with respect to the $–SO_3Na$ function. This study provides new information on how the hydrophilic-headgroup structure influences surfactant performance in w/c systems, particularly regarding hybrid surfactants, and fuels research into low-fluorine-content $CO_2$-philic surfactants.

## 2. Experimental section

### *2.1 Materials*

Synthesis of sulfosuccinate surfactants was previously reported [40, 42]. Sulfoglutarate surfactants were prepared using the same alcohol precursors as used for sulfosuccinate surfactants. The fluorinated and hydrocarbon sulfoglutarate surfactants were synthesized using a Dean and Stark apparatus [39]. Esterification step was included to obtain the hybrid sulfoglutarate surfactant. Further information on the hybrid-sulfoglutarate-surfactant synthesis can be found in section 2.2. Neopentyl alcohol 98% (Acros Organics) and *4H, 4H, 5H, 5H, 5H*-pentafluoropentanol (Apollo Scientific) were used without further purification. Dimethyl

glutaconate ≥ 97% (Sigma Aldrich) was used without further treatment. Maleic anyhidride (99%) and sodium hydrogen sulfide (98%) were obtained from Friendemann Schmidt. *p*-toluene sulfonic acid monohydrate (98%) was obtained from Merck and used as received. Distilled water (Otsuka Pharmaceutical, injection grade, pH = 6.5) and $CO_2$ (Tomoe Shokai, 99.99%) were used as received.

### *2.2 Surfactant synthesis*

#### *2.2.1 Synthesis of hybrid CF2/AOT14GLU diester*

A mixture of dimethyl glutaconate (1.0 eq), 4*H*,4*H*,5*H*,5*H*,5*H* – pentafluoropentanol (1.0 eq), and *p*-toluene sulfonic acid monohydrate (0.1 eq) in toluene (100 ml/5 g dimethyl glutaconate) was reacted overnight under reflux to produce the fluorinated monoester. During the transesterification reaction, methanol was azeotropically liberated to shift the reaction equilibrium and used as an indicator for the reaction completion. After the reaction was considered complete, the CF2-monoester was washed with warm water (70°C). The fluorinated monoester was obtained as yellow transparent liquid after rotary evaporation of the solvent.

To produce the hybrid CF2/AOT14GLU diester, CF2-monoester (1.0 eq) and 2,2-dimethyl propanol (1.0 eq) were dissolved in toluene (10 ml/g monoester) in the presence of *p*-toluene sulfonic monohydrate (0.1 eq). The reaction was performed overnight to remove methanol as a result of the transesterification reaction. Then, the hybrid CF2/AOT14GLU diester was cooled to 70ºC and repeatedly washed with warm water to remove the unreacted *p*-toluene sulfonic monohydrate. The brown crude diester was obtained by rotary evaporation.

#### *2.2.2 Synthesis of the hybrid CF2/AOT14GLU surfactant*

The crude hybrid CF2/AOT14GLU diester (1.0 eq) was dissolved in ethanol (100 ml), and water was added to the mixture until saturation. After sodium hydrogen sulfite (4.0 eq) was added, the reaction mixture was refluxed for 72 h. The reaction was monitored using thin layer chromatography (TLC) eluted with ethyl acetate and considered complete when the diester TLC spot (Rf ~ 0.9) disappeared. The product formation was indicated by the appearance of the baseline surfactant spot (Rf ~ 0). The solvents were evaporated, and a white crude surfactant remained, which was left to dry overnight in an oven at 70°C. Then, the crude surfactant was dissolved in dried acetone and centrifuged to remove any remaining inorganic impurity from the sulfonation step. The pure surfactant was obtained as a white yellowish powder after drying in an oven overnight at 60°C (average yield = 40%).

**Hybrid CF2/AOT14GLU**

$^1$H-NMR (500 MHz, $CDCl_3$, TMS), ($\delta_H$/ppm): 0.88–0.97 (a, s, 9H), 1.86–1.99 (b, m, 2H), 2.08–2.19 (c, m, 2H), 2.56–2.72 (d, m, 2H), 2.98–3.11 (e, m, 2H), 3.70–3.82 (f, m, 4H), 4.08–4.22 (g, m, 1H). Elemental analysis: found C, 36.46; H, 5.17; S, 6.30. Calcd C, 38.80; H, 4.78; S, 6.90.

**di-CF2GLU**

$^1$H-NMR (500 MHz, $(CD_3)_2CO$, TMS), ($\delta_H$/ppm): 1.92–1.98 (a, m, 4H), 2.26–2.37 (b, m, 4H), 2.97 (c, s, 4H), 3.62–3.3.71 (d, m, 4H), 4.19–4.26 (e, m, 1H). Elemental analysis: found C, 32.77; H, 2.58; S, 6.17. Calcd C, 32.50; H, 3.09; S, 5.78.

**AOT14GLU**

$^1$H-NMR (500 MHz, $(CD_3)_2CO$, TMS), ($\delta_H$/ppm): 0.88–0.94 (a, t, 18H, $J$ = 14.85 Hz), 2.66–2.70 (b, dd, 4H, $J$ = 6.85, 16.6 Hz), 3.76–3.78 (c, d, 4H, $J$ = 10.3 Hz), 3.80–3.82 (d, s, 1H). Elemental analysis: found C, 44.59; H, 7.12; S, 9.35. Calcd C, 48.12; H, 7.27; S, 8.56.

*2.3 Surface tension measurements*

Air-water (a/w) surface tensions were measured using a Wilhelmy tensiometer (CBVP-A3, Kyowa Interface Science), which was equipped with a platinum plate. All measurements were performed at 25°C until the surface tension of the surfactant aqueous solutions reached constant values (to avoid any dynamic relaxation effects). Detailed information of the experimental procedures and apparatus are described elsewhere [36, 43]. The critical micelle concentrations (cmc) of each surfactant solution were obtained from the intersection of the graph of the surface tension ($\gamma$) versus ln of concentration (ln c).

*2.4 High-pressure phase behaviour and UV-Visible absorption measurement*

The changes in phase stability of the surfactant/water/$CO_2$ mixtures were visually observed at constant composition with varying temperature and pressure. The measurements were performed at pressures up to 400 bar and controlled temperatures ranging over 35-75°C. The experimental condition was chosen because some surfactants may not exhibit considerable solubility in sc-$CO_2$, this approach is used to achieve surfactant dissolution. A similar procedure has also been used by other groups dealing with $CO_2$-philic surfactants [25, 27, 36, 37]. To obtain comparable results, the surfactant concentration was fixed at 0.24 mol% (~0.05 mol $dm^{-3}$). Meanwhile, to examine the aqueous core formation in w/c microemulsion, UV-Visible absorption spectroscopy measurement with the probe dye methyl orange (MO) solution was performed. The temperature, pressure, surfactant and MO concentration were fixed at 45°C, 400 bar, 0.05 mol $dm^{-3}$ and 0.1 wt % in water, respectively. Predetermined amounts of surfactants and $CO_2$ were loaded into a variable-volume high-pressure optical cell. Then, water or MO solution was added to the surfactant/$CO_2$ mixture until clear Winsor IV microemulsions became turbid macroemulsions. Further information about the experimental procedures and apparatus can be found elsewhere [37, 44].

## 3. RESULTS AND DISCUSSION

### *3.1 Air-water (a/w) surface tension measurement*

**Critical micelle concentrations (cmcs)**. Figure 1 shows the aqueous surface tension data of sulfosuccinate and sulfoglutarate surfactants at 25°C as a function of surfactant concentration. The aqueous properties of each surfactant, which were derived from the surface tension measurements, are shown in Table 2. Previously [23, 29, 35], with several glutarate analogues of fluorinated and hydrocarbon surfactants, it has been shown that the cmc decreases after the $–CH_2$ spacer is added to the surfactant hydrophilic headgroup. However, the decreasing cmc following hydrophilic-headgroup modification does not always follow this simple pattern, because methylene and methyl groups that are added to the surfactant do not contribute equally [45]. The individual cmc between sulfoglutarate and normal sulfosuccinate for the three surfactant classes show the trend of increasing cmc when the headgroup architecture was changed (see Table 2). It is postulated that micelle formation is a result of the balance in tail-water and headgroup-water interactions, although the tails favor aggregation the headgroup remains hydrated [22, 46].

**Limiting surface tension**. One important function of the surfactant is the ability to decrease the air-water surface tension to the limiting value $\gamma_{cmc}$, and this value importantly represents the surfactant effectiveness and is a property of interest for the approximation of w/c microemulsions [15]. Notice that the $\gamma_{cmc}$ values of each surfactant are essentially similar for all surfactants considered (see Table 2). The differences are highly likely within experimental uncertainties (± 0.5 mN $m^{-1}$). Thus, the addition of the $–CH_2$ group on the hydrophilic part exerts much less effect than if it would be placed in the alkyl chain instead [34, 47]. Table 2 shows that the extra $–CH_2$- content in the hydrophilic group does not increase the overall surfactant hydrophobicity. In contrast, a prior study that used a series of linear di-chain

sulfosuccinates, di-C*n*SS (n = 4 - 8), showed that the cmc of surfactants reduced to approximately three fourths for each $–CH_2$ that was added to the surfactant chains [47]. In addition, the increase in total carbon number by adding $–CH_2$- is believed to contribute to the ability of a surfactant in reducing the air-water surface tension [34, 47]. However, the obtained data show one unexpected finding for low-surface-energy materials: the hybrid CF2/AOT14GLU exhibits a notably low $\gamma_{cmc}$ (down to 20.6 mN $m^{-1}$), which is even lower than the fully fluorinated surfactant di-CF2GLU ($\gamma_{cmc}$ = 21.8 mN $m^{-1}$). A double fluorocarbon (FC)-tail surfactant usually has a greater surface-tension-lowering ability than a single FC-tail one of the same FC length, and the $\gamma_{cmc}$ value of the hybrid CF2/AOT14GLU was expected to be between those of di-CF2GLU and AOT14GLU. It may be expected that the ability of the hybrid CF2/AOT14GLU to stabilize w/c microemulsions is enhanced because this surfactant also proves to be notably efficient in decreasing air-water surface tension.

**Surfactant coverage at the a/w interface.** An important parameter characterizing the area covered by the surfactant molecule is the effective area occupied per surfactant molecule at the cmc ($A_{cmc}/Å^2$). It is a measure for the coverage area occupied by one surfactant molecule at the air-water interface and is obtained from the tensiometric analysis which can be found in detail at the supplementary material. The pre-cmc data were fitted to quadratic functions to generate adsorption isotherms using Gibbs equation (Eq. 1); thus, the areas per headgroup at the cmc ($A_{cmc}$) were calculated. The prefactor m = 2 is responsible for the ratio 1:1 of dissociating ions for ionic surfactants.

$$\Gamma = -\frac{1}{mRT}\frac{d\gamma}{d\ln c} \qquad (1)$$

$$A_{cmc} = \frac{1}{\Gamma N_A} \qquad (2)$$

For all cases, the sulfoglutarate surfactants exhibit notably larger $A_{cmc}$ than sulfosuccinates, which follows the similar observed trends for hydrocarbon and fluorinated sulfoglutarate surfactants [29, 35, 38]. Considering that these two surfactant classes differ only in headgroup architecture, the changes in $A_{cmc}$ can be ascribed to the effect of adding an extra $–CH_2-$ to the surfactant hydrophilic part. Because of the presence of the $–CH_2-$ spacer in the surfactant headgroup, the glutarate surfactants have slightly larger headgroups [48]. Moreover, the double tails of the sulfoglutarate surfactant may be more open than those of the sulfosuccinates because of the extra linking spacer in the hydrophilic group [29, 35, 36]. These factors may cause the sulfoglutarate surfactants to occupy larger areas at the interface.

### *3.2 High-pressure phase behaviour*

In $CO_2$ studies, high-pressure phase behaviour is necessary to seek the optimum conditions for stabilizing water-in-$CO_2$ microemulsions. Here, to readily compare the performance of all surfactants, a fixed surfactant concentration and water-to-surfactant molar ratio (*w*) were used. The value $P_{trans}$ is the lowest pressure for a given composition and temperature at which the microemulsions remain single transparent one phase systems (1Φ); below $P_{trans}$ phase separation occurs and the systems become turbid, indicating the formation of macroemulsions (2Φ). Hence, $P_{trans}$ was used to evaluate the ability of the $CO_2$-philic surfactants to stabilize w/c microemulsions: the phase behaviour and $P_{trans}$ values for the surfactants in this study are shown in Figure 2 and Table 2, respectively.

Attempts to disperse water in dense $CO_2$ using both sulfosuccinate and sulfoglutarate versions of hydrocarbon surfactants (AOT14 and AOT14GLU) did not produce single transparent phases under the experimental conditions used here. Hence, the data for these two surfactants are not included in the phase diagram. Earlier studies on the identical system also reported the inability of the AOT14 surfactant to stabilize w/c microemulsions [42] despite the

versatility of the parent AOT14; which is the tri-chain TC14 surfactant, in a wide range of solvents [41, 49]. However, changing the hydrophilic headgroup into the larger sulfoglutarate was not sufficient to increase the tendency of the surfactants to stabilize w/c microemulsions. Previous work that used hydrocarbon sulfoglutarate surfactants focused on water-in-oil (w/o) microemulsion system and low-surface-energy materials [29, 35].

As expected, the fully fluorinated surfactant di-CF2 exhibits the lowest $P_{trans}$ among the surfactants investigated in this study. Molecular simulation studies suggested that fluorination on the surfactant chains is the key factor for producing favorable interaction with $CO_2$ via quadrupolar and dispersion interactions between the surfactant tails and $CO_2$. Moreover, fluorocarbon chains are less attractive to each other than hydrocarbon counterparts, making them are more $CO_2$-philic [13-15, 31, 40]. Here, the use of the sulfoglutarate surfactant di-CF2GLU increases $P_{trans}$ by approximately 30 bar at 55°C. However, the difference is small, considering the uncertainties of approximately 20-40 bar. Earlier studies by Sagisaka et al. [37, 38] also reported the minor difference in $P_{trans}$ when exchanging sulfosuccinate with the sulfoglutarate headgroup for all examined fluorinated surfactants.

For hybrid surfactants, exchanging sulfosuccinate with the sulfoglutarate headgroup significantly affects the stabilization of the w/c microemulsion systems. Compared with the hybrid CF2/AOT14 ($P_{trans}$ = 383 bar), the extra $–CH_2-$ content in the hybrid CF2/AOT14GLU ($P_{trans}$ = 232 bar) decreases $P_{trans}$ to approximately 150 bar at 55°C, which even approaches the level of the fully-fluorinated surfactant di-CF2 (219 bar). The significant improvement of the hybrid CF2/AOT14GLU may be related to high interfacial activity at the water-$CO_2$ interface. Returning to the data of $\gamma_{cmc}$ in Table 2, the hybrid CF2/AOT14GLU exhibits the lowest values, which illustrates high effectivity in reducing the air-water surface tension and consequently the water-$CO_2$ interfacial tension [36]. This result is consistent with the arguments in [15],

suggesting that surfactants with lower $\gamma_{cmc}$ will be expected to stabilize w/c microemulsions formation at lower $P_{trans}$ values.

### *3.3 UV-Visible spectroscopy measurement of w/c microemulsions*

To gain evidence for w/c microemulsion formation, the presence of reverse micelles in sc-$CO_2$ was shown by determining the incorporation a polar water-soluble probe dye methyl orange (MO) in the water/surfactant/$CO_2$ systems. (MO is insoluble in sc-$CO_2$ and soluble in water.) The existence of reverse micelles in sc-$CO_2$ is indicated by the red dyed single-phase mixtures because the MO dissolves inside surfactant-stabilized water pools of the $CO_2$ continuous phase [44]. The UV-visible absorption spectra of MO in the water/surfactant/$CO_2$ systems are shown in Figure 3. With the aforementioned phase behaviour studies, the fluorinated surfactants di-CF2 exhibit the highest and MO broad peak absorbance. The comparisons among hybrid surfactants show that the sulfoglutarate version provides better $CO_2$-compatibility, as reflected by the higher absorbance of the hybrid CF2/AOT14GLU.

The solubilization of MO in water-$CO_2$ microemulsions is expected to display a linear relationship for MO absorbance and *w* up to a certain *w* value, as shown in Figure 4. As observed, the increase in *w* gradually decreases, which suggests the phase transition from Winsor IV (1Φ) to Winsor II (2Φ) microemulsions. Following the similar lines [36-38], the trend of increasing solubilizing power is also observed when sulfosuccinate is changed for sulfoglutarate. For a $CO_2$-philic surfactant to have high solubilizing power, structural disorder in the surfactant molecular structure is required to decrease the length-to-breadth ratio, which decreases the possibility of liquid-crystal-like formation [36, 50]. Although $w_{max}$ is larger for the nFG$(EO)_2$ series [36-38], here, the sulfoglutarate version provides slightly higher solubilizing power than the normal sulfosuccinates di-CF2 ($w_{max}$ = 10) and hybrid CF2/AOT14 ($w_{max}$ = 3). Using the sulfoglutarate surfactant increases the solubilizing power of di-CF2GLU

and hybrid CF2/AOT14GLU to $w_{max}$ = 13 and $w_{max}$ = 7, respectively. Instead of enhancing the surfactant solubilizing power, swapping sulfosuccinate for the sulfoglutarate headgroup affects the surfactant efficiency in stabilizing the w/c microemulsion more, particularly with the hybrid surfactant.

## 4. Conclusions

To further explore the molecular design requirements for $CO_2$-philic surfactants, three classes of custom-made AOT-derived surfactant–sulfoglutarate surfactants were successfully synthesized. All results show that the extra $–CH_2$ content in the surfactant headgroup causes different effects for different surfactant types. The differences in $P_{trans}$ and $\gamma_{cmc}$ are indeed subtle considering the involved uncertainties. Conversely, a significant $–CH_2$- head group spacer effect was observed for the hybrid surfactants. The hybrid CF2/AOT14GLU is more $CO_2$-philic than the parent hybrid CF2/AOT14 as indicated by the lower $P_{trans}$ and $\gamma_{cmc}$ values. Not all $–CH_2$- groups that are added to the hydrophilic headgroup contribute equally to the surfactant $CO_2$-philicity. The obtained results may be used as a reference to design a new generation of low-fluorine-content-based $CO_2$-philic surfactants.

Azmi – add some (3 -6) of the references in to the conclusions section – show how your new results compare with published literature

This is important

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